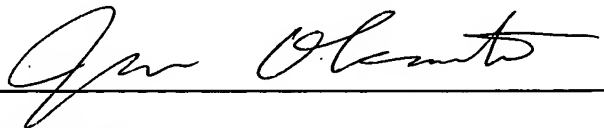


DECLARATION

I, Jun OKAMOTO, residing at 2023, Takao-machi, Hachioji-shi, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/436,631 filed on December 30, 2002.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 2nd day of October, 2003

A handwritten signature in cursive script, appearing to read "Jun Okamoto", is written over a horizontal line.

Jun OKAMOTO

10/540560

JCT7REC-010110 24 JUN 2005

[Document Name] Specification
[Title of the Invention] Vapor Grown Carbon Fiber and
Use Thereof
[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to an electrically conductive composition which is employed in electronic materials, which is employed, as a wiring material or a material for connecting devices, in a variety of industrial products, including integrated circuits, electronic parts, optical parts, and various control parts, which is employed as an antistatic material or an electromagnetic wave shielding material in a variety of devices, and which is employed for, for example, antistatic coating; to an electrically conductive coating material containing the composition; and to an electrically conductive adhesive containing the composition.

[0002]

[Background Art]

An electrically conductive coating material or an electrically conductive adhesive is in the form of, for example, an electrically conductive paste product. Depending on the use, the electrically conductive paste product is narrowly classified into an electrically conductive paste and a resistor paste. In the present invention, the term "electrically conductive paste" encompasses a resistor paste.

An electrically conductive paste predominantly contains an electrically conductive material, an auxiliary agent, a resin serving as a binder or a matrix material, and a solvent, and is prepared by dispersing fine particles of the electrically conductive material and the auxiliary agent into a varnish obtained by dissolving the resin in the solvent. Dispersion of the electrically conductive material and the auxiliary agent is performed by use of a dispersion mixing machine, a pulverizer, or a mill; specifically, a three roll mill, a ball mill, a paint shaker, or a planetary mill. Depending on the temperature required for thermal treatment after application, the electrically conductive paste is classified into a paste which is cured through drying (hereinafter may be referred to as a "drying-cured paste") and a paste which is cured through baking (hereinafter may be referred to as a "baking-cured paste").

[0003]

A drying-cured paste is thermally treated at a temperature falling within a range of ambient temperature to about 250°C, to thereby form a composite product containing the electrically conductive material, the auxiliary agent, and the resin component. When the resin to be employed in the drying-cured paste is appropriately chosen, characteristics (e.g., solvent resistance, thermal resistance, adhesion, and flexibility) can be imparted to the paste. Typical examples of the resin employed in the paste include phenolic resin, epoxy resin, polyester resin, silicone resin,

acrylic resin, and polypropylene resin. When a baking-cured paste is thermally treated at a temperature of about 400°C to about 1,300°C after application, the organic component of the paste is burned out, and the inorganic component remains in the thus-treated paste. The resin employed in the baking-cured paste is chosen in consideration of behavior of the resin during the course of application or thermal treatment of the paste. Examples of the resin employed in the paste include cellulose resins such as nitrocellulose and ethyl cellulose, acrylic resin, and butyral resin.

[0004]

In order to improve fluidity of the paste during the course of application, and to improve the strength and tribological characteristics of a coating film formed through application of the paste, a dispersant or a thickener is employed as the auxiliary agent. Examples of the auxiliary agent employed include silicon oxide and alumina.

The solvent must be chosen in consideration of the solubility of the resin in the solvent, the fluidity of the solvent required for dispersing the electrically conductive material therein, the volatility of the solvent during the course of thermal treatment of the paste performed after application, and characteristics of a coating film formed after volatilization of the solvent. Examples of the solvent employed include methyl ethyl ketone, N-methylpyrrolidone, terpene compounds such as terpineol, glycol ethers, and glycol esters.

[0005]

Application of such an electrically conductive paste is performed by means of screen printing, the dispenser method, dipping, the transfer method, the applicator method, brush application, or spraying. When the paste is applied to a substrate or an electronic element, generally, screen printing, dipping, or the transfer method is employed. In accordance with the application method to be employed, the viscosity, etc. of the electrically conductive paste must be regulated.

[0006]

As the electrically conductive material, there are employed fine particles of a noble metal or a noble metal alloy, such as gold, platinum, palladium, silver, a silver-platinum alloy, or a silver-palladium alloy, or fine particles of a base metal such as copper, nickel, aluminum, or tungsten. Alternatively, there are employed fine particles of an electrically conductive non-metallic material such as carbon, graphite, carbon black, ruthenium oxide, tin oxide, or tantalum oxide.

[0007]

However, the electrically conductive paste containing a metal serving as the electrically conductive material involves the following problems: electrical conductivity is lowered with passage of time through, for example, oxidation or corrosion of the metal; an electrically conductive coating film formed of the conductive paste is exfoliated from an

electric circuit board because of deformation of the circuit board; and the conductive paste is expensive when the metal is silver. Meanwhile, the carbon-containing electrically conductive material involves problems in that, for example, its electrical conductivity is insufficient, although the conductive material exhibits resistance against, for example, oxidation and corrosion, and is advantageous from the economical viewpoint.

[0008]

Recently, there have been proposed an electrically conductive coating material containing vapor grown carbon fiber, carbon black, and a thermoplastic resin and/or a thermosetting resin (see, for example, Patent Document 1); an electrically conductive coating material containing boron-containing fine carbon fiber, and a thermoplastic resin or a thermosetting resin (see, for example, Patent Document 2); and a coating material containing carbon fiber which is readily graphitized, or an adhesive containing the carbon fiber (see, for example, Patent Document 3).

[0009]

[Patent Document 1] Japanese Patent Application Laid-Open (*kokai*) No. 6-122785.

[0010]

[Patent Document 2] Japanese Patent Application Laid-Open (*kokai*) No. 2001-200211.

[0011]

[Patent Document 3] Japanese Patent Application Laid-

Open (kokai) No. 61-218669.

[0012]

[Problems to be Solved by the Invention]

In general, an electrically conductive coating material or an electrically conductive adhesive incorporates, as an electrically conductive material, fine particles of a noble metal such as silver, gold, or platinum, fine particles of a base metal such as copper or nickel, or fine particles of carbon. In contrast, Patent Documents 1 through 3 propose a technique in which an electrically conductive composition containing a resin component and carbon fiber is employed, to thereby provide an electrically conductive coating material or an electrically conductive adhesive, which exhibits improved characteristics (e.g., electrical conductivity and durability).

However, in the technique proposed in any of the above documents, a large amount of carbon fiber must be added to the resin component in order to obtain sufficient electrical conductivity. As a result, a mixture of the carbon fiber and the resin component exhibits lowered fluidity. Meanwhile, when merely graphitized carbon fiber is employed as an electrically conductive component, the resultant electrically conductive composition exhibits resistance anisotropy.

[0013]

Objects of the present invention are to provide an electrically conductive coating material or an electrically conductive adhesive, which contains an electrically

conductive composition exhibiting improved electrical conductivity, migration prevention, oxidation resistance, stability over years (hereinafter may be referred to as "long-term stability"), and tribological characteristics; and to provide a coating film (electrically conductive product) containing the coating material or the adhesive and exhibiting low resistance anisotropy.

The electrically conductive coating material or electrically conductive adhesive of the present invention exhibits excellent thermal conductivity in addition to electrical conductivity, and thus provides a material endowed with heat release property.

[0014]

[Means for Solving the Problems]

In order to solve the aforementioned problems, the present inventors have developed a carbonaceous material for forming an electrically conductive composition, which contains, as an electrically conductive material, vapor grown carbon fiber and graphitic particles and/or amorphous carbon particles; an electrically conductive composition containing the carbonaceous material; and an electrically conductive coating material or an electrically conductive adhesive, which contains the composition.

The present inventors have also developed a carbonaceous material for forming an electrically conductive composition, which is a mixture of vapor grown carbon fiber containing boron in an amount of 0.01 to 5 mass% and

graphitic particles and/or amorphous carbon particles, wherein the amount of the carbon fiber is 20 mass% or more; an electrically conductive composition containing the carbonaceous material; and an electrically conductive coating material or an electrically conductive adhesive, which contains the composition.

The electrically conductive coating material or electrically conductive adhesive of the present invention exhibits excellent thermal conductivity in addition to electrical conductivity, and thus provides a material endowed with heat release property.

The electrically conductive coating material assumes the form of a liquid, paste-like, or powdery product. When the conductive coating material having a fluid form is applied to the surface of an object, a thin film is formed on the surface, and, with passage of time, the thin film adheres to the surface and becomes a solid film (coating film), to thereby attain continuous coverage of the surface. The fluid form encompasses a liquid, a melt, and an air-borne suspension.

[0015]

In order to solve the aforementioned problems, the present invention provides the following.

[1] A carbonaceous material for forming an electrically conductive composition, comprising a mixture of a vapor grown carbon fiber, and graphitic particles and/or amorphous carbon particles, each fiber filament of the carbon fiber containing

a hollow space along the filament in its interior and having a multi-layer structure, an outer diameter of 2 to 500 nm, and an aspect ratio of 10 to 15,000, wherein the amount of the vapor grown carbon fiber is 10 to 90 mass%, the amount of the graphitic particles is 7 to 65 mass%, and the amount of the amorphous carbon particles is 7 to 35 mass%.

[2] A carbonaceous material for forming an electrically conductive composition according to claim 1, which is a mixture of the vapor grown carbon fiber, and the graphitic particles and/or the amorphous carbon particles, each fiber filament of the carbon fiber containing a hollow space along the filament in its interior and having a multi-layer structure, an outer diameter of 2 to 500 nm, and an aspect ratio of 10 to 15,000, wherein the carbon fiber contains boron in an amount of 0.01 to 5 mass%, and the amount of the carbon fiber in the carbonaceous material is at least 20 mass%.

[0016]

[3] A carbonaceous material for forming an electrically conductive composition according to [1] or [2] above, wherein the vapor grown carbon fiber contains a branched, vapor grown carbon fiber.

[4] A carbonaceous material for forming an electrically conductive composition according to any of [1] through [3] above, wherein the vapor grown carbon fiber contains a nodular, vapor grown carbon fiber.

[0017]

[5] A carbonaceous material for forming an electrically conductive composition according to any of [1] through [4] above, wherein the graphitic particles or the amorphous carbon particles have an average particle size of 0.1 to 100 μm .

[6] A carbonaceous material for forming an electrically conductive composition according to any of [1] through [5] above, wherein the graphitic particles or the amorphous carbon particles have been thermally treated at 2,000°C or higher.

[7] A carbonaceous material for forming an electrically conductive composition according to any of [1] through [6] above, wherein the graphitic particles contain boron.

[0018]

[8] A carbonaceous material for forming an electrically conductive composition according to [1] or [2] above, wherein the amorphous carbon particles are formed of carbon black or glassy carbon.

[9] A carbonaceous material for forming an electrically conductive composition according to [8] above, wherein the carbon black is at least one species selected from the group consisting of oil furnace black, gas black, acetylene black, lamp black, thermal black, channel black, and Ketjenblack.

[10] An electrically conductive composition comprising a carbonaceous material as recited in any of [1] through [9] above and a resin component serving as a binder or a matrix material, and, if desired, a solvent.

[11] An electrically conductive composition according to [10] above, wherein, when a mass%, b mass%, and c mass% represent the amounts of the vapor grown carbon fiber, the graphitic particles, and the amorphous carbon particles contained in the composition, with the proviso that the solvent being excluded from the composition, respectively, a, b, and c satisfy the following relations:

$5 \leq a + b + c \leq 80$, $1 \leq a \leq 60$, $1 \leq b \leq 60$, and $1 \leq c \leq 30$.

[0019]

[12] A method for producing an electrically conductive composition characterized by comprising adding a resin component and, if desired, a solvent to a carbonaceous material for forming an electrically conductive composition as recited in any of [1] through [11] above, and kneading the resultant mixture.

[13] An electrically conductive coating material characterized by comprising, as an electrically conductive material, an electrically conductive composition as recited in any of [1] through [11] above.

[14] An electrically conductive coating material according to [13] above, which is employed as an electrically conductive paste.

[0020]

[15] An electrically conductive adhesive characterized by comprising an electrically conductive composition as recited in [10] or [11] above.

[16] An electrically conductive coating film characterized by being formed by use of an electrically conductive coating material as recited in [13] above.

[17] An electronic part characterized by being formed by use of an electrically conductive coating material as recited in [13] above and/or an electrically conductive adhesive as recited in [15] above.

[0021]

[Modes for Carrying Out the Invention]

The present invention will next be described in detail.

(Vapor grown carbon fiber)

In the late 1980's, studies were performed on vapor grown carbon fiber. Carbon fiber, each fiber filament of the fiber having a diameter of several nm to 1,000 nm inclusive, is known to be produced through thermal decomposition of a gas of, for example, hydrocarbon in a vapor phase in the presence of a metallic catalyst.

[0022]

A variety of processes for producing vapor grown carbon fiber are disclosed, including a process in which an organic compound such as benzene, serving as a raw material, and an organo-transition metallic compound such as ferrocene, serving as a catalyst, are brought into a high-temperature reaction furnace together with a carrier gas, to thereby produce vapor grown carbon fiber on a substrate (Japanese Patent Application Laid-Open (*kokai*) No. 60-27700); a process in which vapor grown carbon fiber is produced in a dispersed

state (Japanese Patent Application Laid-Open (*kokai*) No. 60-54998); and a process in which vapor grown carbon fiber is produced on a reaction furnace wall (Japanese Patent Application Laid-Open (*kokai*) No. 7-150419). Vapor grown carbon fiber produced through any of the above processes is thermally treated in an inert atmosphere (e.g., argon) at 600 to 1,500°C, and further thermally treated at 2,000 to 3,300°C, to thereby graphitize the carbon fiber (Japanese Patent Application Laid-Open (*kokai*) No. 8-60444).

[0023]

Through the aforementioned processes, there can be produced carbon fiber of relatively small diameter and high aspect ratio which exhibits excellent electrical conductivity and thermal conductivity, and is suitable as a filler material. Therefore, carbon fiber, each fiber filament of the fiber having a diameter of about 2 to about 500 nm and an aspect ratio of about 10 to about 15,000, is mass-produced, and is employed, for example, as an electrically or thermally conductive filler material in electrically conductive resin or as an additive in lead storage batteries.

[0024]

A characteristic feature of a vapor grown carbon fiber filament resides in its shape and crystal structure. The filament has a structure including a very thin hollow space extending along the filament in its center portion, and a plurality of carbon hexagonal network layers grown around the hollow space so as to form concentric rings. The vapor grown

carbon fiber employed in the present invention may be, for example, branched, vapor-grown carbon fiber disclosed in Japanese Patent Application Laid-Open (*kokai*) No. 2002-266170, or vapor grown carbon fiber having a nodular portion, in which the diameter of each fiber filament of the carbon fiber differs from portion to portion.

[0025]

(Boron-containing carbon fiber)

In order to further enhance the electrical conductivity of vapor grown carbon fiber as described above, the crystallinity (graphitization degree) of the carbon fiber is enhanced by use of a graphitization catalyst. For example, when the vapor grown carbon fiber is graphitized by use of boron and/or a boron compound, serving as a graphitization catalyst, the resultant carbon fiber (boron-containing carbon fiber), which contains boron, or boron and the boron compound, exhibits electrical conductivity higher than that of general vapor grown carbon fiber.

[0026]

"As-produced" vapor grown carbon fiber serves as a carbonaceous material having high electrical conductivity, and an electrically conductive composition containing the carbon fiber exhibits high mechanical strength. However, as-produced vapor grown carbon fiber may have, on its surface, for example, a hydrocarbon (i.e., a raw material of the carbon fiber) and products formed through thermal decomposition of the hydrocarbon, and, in many cases, the

carbon fiber exhibits insufficient crystallinity. When such as-produced carbon fiber is thermally treated in an inert atmosphere at 2,000°C (preferably at 2,300°C or higher), thermal decomposition products adhering to the carbon fiber are volatilized and removed therefrom, and crystallization (graphitization) of the carbon fiber proceeds, whereby the electrical conductivity of the carbon fiber can be enhanced. When the crystallinity of the carbon fiber is enhanced, the electrical conductivity thereof is also enhanced, which is preferable. Thermally treating the carbon fiber in the presence of boron is particularly preferred, since graphitization of the carbon fiber is promoted.

[0027]

Boron-containing vapor grown carbon fiber is produced through the following procedure: the aforementioned vapor grown carbon fiber; branched, vapor grown carbon fiber; or nodular, vapor grown carbon fiber is thermally treated by means of, for example, the method disclosed in International Publication WO/00/58536 pamphlet in an inert atmosphere (e.g., argon) at 2,000 to 3,300°C in the presence of boron or a boron compound such as boric acid, a borate, boron oxide, or boron carbide.

[0028]

As the raw material of the boron-containing carbon fiber, there is employed fine vapor grown carbon fiber of low crystallinity which has been thermally treated at a low temperature and which is readily doped with boron; for

example, vapor grown carbon fiber which has been thermally treated at 1,500°C or lower (preferably, as-produced (as-grown) vapor grown carbon fiber which has not undergone thermal treatment). Even when carbon fiber which has not undergone thermal treatment is employed, the carbon fiber is heated up to the graphitization temperature during the course of thermal treatment employing a boron catalyst (boronization). Therefore, carbon fiber of low crystallinity can be employed as the raw material. The raw material of the boron-containing carbon fiber may be carbon fiber which has been graphitized at 2,000°C or higher, or at 2,300°C or higher at which general thermal treatment is performed. However, from the viewpoint of energy saving, carbon fiber to be employed as the raw material has not necessarily been graphitized in advance, and preferably, carbon fiber which has not undergone thermal treatment is employed so that boron exhibits its catalytic effect.

[0029]

Fine carbon fiber serving as the raw material of the boron-containing carbon fiber may be pulverized or milled in advance, in order to improve its handling. However, in view that a filler formation treatment, such as pulverization, milling, or classification, will eventually be performed as a final step after the raw material carbon fiber is thermally treated in the presence of a boron compound or boron (but without allowing the carbon fiber to be brought into direct contact with the boron compound or boron), the length of the

raw material carbon fiber is not necessarily required to be regulated to a length suitable for providing, for example, a filler before thermal treatment of the carbon fiber. Carbon fiber which is generally produced through a vapor growth process, each fiber filament of the carbon fiber having a diameter of about 2 to about 1,000 nm and a length of about 500 to about 400,000 nm, may be employed as the raw material carbon fiber without any treatment. Such carbon fiber serving as the raw material may have a "flocky" appearance. The raw material carbon fiber to undergo boronization may be thermally treated, and in this case, the thermal treatment temperature is preferably 1,500°C or lower.

[0030]

The boron compound to be employed for thermal treatment preferably has the following physical properties. Since thermal treatment is performed at a temperature of 2,000°C or higher, the boron compound to be employed must be a substance that is not evaporated through, for example, decomposition before the thermal treatment temperature reaches 2,000°C. Examples of the boron compound to be employed include elemental boron; boron oxides such as B_2O_2 , B_2O_3 , B_4O_3 , and B_4O_5 ; boric acids such as orthoboric acid, metaboric acid, and tetraboric acid, and salts of boric acids; boron carbides such as B_4C and B_6C ; and BN. Boron carbides such as B_4C and B_6C and elemental boron are preferred.

[0031]

Examples of the method for doping carbon fiber with

boron include a method in which a boron compound or boron is added directly to or mixed with carbon fiber; and a method in which carbon fiber is doped with a boron compound or boron such that they are not brought into contact with each other.

The doping amount of boron is generally 0.01 mass% to 5 mass% on the basis of the entire amount of carbon fiber. Therefore, when a boron compound or boron is caused to coexist with carbon fiber such that they are not brought into direct contact with each other, in consideration of percent conversion, the amount of the boron compound or boron to be employed is regulated to 5 mass% or more as reduced to atomic boron on the basis of the entire amount of carbon. When the amount of boron to be employed is small, the effect of boron is insufficiently obtained.

[0032]

In the case where a boron compound or boron is added directly to or mixed with carbon fiber, during the course of thermal treatment, an excess amount of the boron compound or boron tends to be melted and sintered on the carbon fiber, and thus the boron compound or boron solidifies or covers the surface of the carbon fiber, whereby characteristics of the carbon fiber required for forming a filler are deteriorated (for example, the electrical resistance of the carbon fiber increases). Particularly when a transition metallic compound—which is formed into a catalyst seed to be employed during the course of production of carbon fiber—or a metallic component derived from the compound

reacts with boron, to thereby form a boride (metal boride), which is readily liquefied in crystals of the carbon fiber or on the surface of the carbon fiber, preferably, the carbon fiber is not brought into contact with the boron compound or boron.

[0033]

Such fine carbon fiber serving as the raw material of the boron-containing carbon fiber has a three-dimensional structure, tends to form a flock, and has very low bulk density and very high porosity. In addition, since the amount of boron to be added to the raw material carbon fiber is very small, difficulty is encountered in bringing boron and the carbon fiber into contact with each other uniformly by merely mixing them. As a result, the added boron is difficult to exhibit its catalytic effect throughout the carbon fiber uniformly.

[0034]

In order to efficiently introduce boron into the raw material carbon fiber by bringing the carbon fiber into contact with a boron compound or boron, the carbon fiber and the boron compound or boron must be sufficiently mixed together, to thereby bring the carbon fiber into contact with the boron compound or boron as uniformly as possible. In order to attain such uniform contact, preferably, particles of the boron compound or boron having a possibly minimum particle size are employed. In the case where the carbon fiber is not brought into contact with the boron compound or

boron, no particular limitations are imposed on the size of the carbon fiber. Even when the carbon fiber has a large size, a portion containing boron of high concentration is not formed on the carbon fiber, and formation of solidified mass of boron tends not to occur.

[0035]

In general, fine carbon fiber produced through a vapor phase process has low bulk density. For example, an as-produced fine carbon fiber aggregate has a bulk density of about 0.01 g/cm^3 or less, and even when the aggregate is subjected to thermal treatment, pulverization, milling, and classification, the resultant product has a bulk density of about 0.02 to about 0.08 g/cm^3 . Since such fine carbon fiber has high porosity, when the carbon fiber is thermally treated, a thermal treatment furnace of very large capacity is required, leading to high equipment cost and low productivity. Therefore, unlike the case where boron is introduced into a general carbon material, an efficient process is required for introducing boron into such fine carbon fiber.

[0036]

In order to efficiently introduce boron into carbon fiber, the concentration of boron present around the carbon fiber must be sufficiently maintained. In order to maintain the boron concentration, the carbon fiber and boron must be brought into direct contact with each other. However, when boron reacts with a metallic catalyst (e.g., iron or cobalt) employed for producing vapor grown carbon fiber, to thereby

form a boride, an excess amount of the boride remains in the resultant carbon fiber, and use characteristics of the carbon fiber are deteriorated, direct contact between the carbon fiber and boron must be prevented, and uniform distribution of the boron concentration must be achieved during the course of thermal treatment of the carbon fiber.

[0037]

Thus, in order to prevent direct contact between the carbon fiber and a boron compound or boron, which are in the form of solid, before thermal treatment, the carbon fiber and the boron compound or boron may be placed in separate containers (e.g., crucibles), for example, or the boron compound or boron may be wrapped with carbon fiber cloth, to thereby cause them to coexist, followed by thermal treatment of the carbon fiber. Preferably, thermal treatment is carried out after the carbon fiber is densified, so that the density of the carbon fiber is maintained as high as possible. In a preferred method for attaining such densification, before thermal treatment, a container containing the boron compound or boron is placed into a container filled with the carbon fiber, and subsequently pressure is applied to the carbon-fiber containing container so as to compress the container, thereby densifying the carbon fiber and maintaining the density of the carbon fiber at a high level.

[0038]

As described above, the raw material carbon fiber to be employed may be as-produced carbon fiber or a product

obtained by thermally treating the as-produced carbon fiber at 1,500°C or lower. However, from the viewpoints of cost and performance, preferably, as-produced carbon fiber is employed.

In order to increase the density of a mixture of carbon fiber and a boron compound or boron, and maintain the density of the mixture at high level, there may be employed any of the following methods: a shaping method; a granulation method; and a method in which a mixture of the carbon fiber and the boron compound or boron is placed into a crucible, and the mixture is compressed into a compact of predetermined shape. In the case where the shaping method is employed, the resultant shaped product may assume any shape selected from among a columnar shape, a plate-like shape, and a rectangular parallelepiped shape.

[0039]

When the mixture of the carbon fiber and the boron compound or boron is compressed to thereby form a compact, and then pressure applied to the mixture is released, the volume of the compact may increase to some extent, whereby the bulk density of the compact may decrease. In such a case, the bulk density of the compact during the course of compression is regulated such that the bulk density of the compact after release of the applied pressure becomes 0.03 g/cm³ or more. In the case where the carbon fiber is placed in a container, in order to enhance treatment efficiency, the carbon fiber may be compressed by use of, for example, a

pressurizing plate so as to attain a bulk density of 0.03 g/cm³ or more. Alternatively, while being compressed, the carbon fiber may be subjected to thermal treatment.

[0040]

The thermal treatment temperature required for introducing boron into carbon crystals is 2,000°C or higher, preferably 2,300°C or higher. When the treatment temperature is below 2,000°C, introduction of boron becomes difficult, because of low reactivity between boron and carbon. In order to further promote introduction of boron, to enhance crystallinity of carbon fiber, and particularly to regulate the interlayer distance (d_{002}) of hexagonal carbon layers of carbon fiber, each fiber filament of the carbon fiber having a diameter of about 100 nm, to 0.3385 nm or less, the treatment temperature is preferably maintained at 2,300°C or higher. No particular limitations are imposed on the upper limit of the thermal treatment temperature. However, in consideration of the upper limit of the temperature of an apparatus to be employed, the upper limit of the thermal treatment temperature is about 3,200°C.

[0041]

No particular limitations are imposed on the thermal treatment furnace to be employed, so long as the furnace can maintain a target temperature of 2,000°C or higher, preferably 2,300°C or higher. The thermal treatment furnace may be any of generally employed furnaces, such as an Acheson furnace, a resistive furnace, and a high-frequency furnace.

In some cases, thermal treatment may be carried out by applying electricity directly to a powdery or shaped carbon fiber product, to thereby heat the product.

[0042]

Thermal treatment is carried out in a non-oxidative atmosphere, preferably in an atmosphere containing one or more rare gases selected from among argon, helium, and neon. From the viewpoint of productivity, the thermal treatment time is preferably shortened to a possibly minimum level. Particularly when heat treatment is carried out for a long period of time, sintering and solidification of carbon fiber proceeds, resulting in low product yield. Therefore, after the temperature of the center portion of, for example, a shaped carbon fiber product reaches the target temperature, the product is maintained at the target temperature within one hour. Such a maintenance time is sufficient for thermal treatment of carbon fiber.

[0043]

(Amorphous carbon particles)

The term "amorphous carbon" refers to a carbon material having a three-dimensional structure in which carbon atoms are irregularly arranged. When amorphous carbon material is subjected to X-ray diffractometry or electron diffractometry, a broad reflection peak is obtained. Examples of the amorphous carbon material include glassy carbon, carbon black, and a carbon material of low crystallinity which has undergone thermal treatment at a low temperature and has

neither a three-dimensional regular structure nor a graphite structure.

[0044]

Of these, carbon black contains amorphous carbon in an amount of about 95% or more, and is in the form of fine particles whose size is in the order of nm. Carbon black is a carbon material exhibiting good quality in terms of, for example, specific surface area, microstructure, and aggregate distribution, and is suitable for use in the present invention.

[0045]

There have been known various types of carbon black, which are produced from different raw materials by means of different production methods. Examples of the carbon black which is suitable for use in the present invention include oil furnace black, gas black, acetylene black, lamp black, thermal black, channel black, and Ketjenblack. Of these, acetylene black, thermal black, channel black, and Ketjenblack are preferred.

[0046]

Preferably, amorphous carbon particles employed in the present invention (for example, carbon black particles), have a well-developed structure; have a small primary particle size, a large secondary particle size, and a large surface area; and are porous. The amorphous carbon particles preferably attain an oil supply of 90 ml(DBP)/100 g or more. This is because when the amorphous carbon particles exhibit

the above characteristics, the particles readily form a microstructure and exhibit higher electrical conductivity.

The particle size of each of the amorphous carbon particles (on the basis of microstructure) is generally 30 to 500 nm, preferably 30 to 100 nm. The BET specific surface area of the particles is preferably 20 to 50 m²/g.

[0047]

The amount of the amorphous carbon particles contained in the carbonaceous material for forming an electrically conductive composition of the present invention is generally 7 to 35 mass%, preferably 10 to 30 mass%.

When the amount of the amorphous carbon particles contained in the electrically conductive composition is 1 to 60 mass%, preferably 2 to 30 mass%, more preferably 5 to 20 mass%. When the amount of the amorphous carbon particles is less than 1 mass%, the electrically conductive composition may fail to exhibit sufficient electrical conductivity and low resistance anisotropy, whereas when the amount of the amorphous carbon particles is 60 mass% or more, the amount of the vapor grown carbon fiber or graphitic particles becomes relatively small, or the amount of the resin component becomes small, and thus the composition may fail to exhibit sufficient electrical conductivity.

[0048]

The amorphous carbon particles (e.g., carbon black) may be employed without any treatment. Alternatively, as in the case of the vapor grown carbon fiber, the amorphous carbon

particles may be thermally treated at 2,000°C or higher (preferably at 2,300°C or higher), or may be thermally treated in the presence of a boron compound or boron at 2,000°C or higher (preferably at 2,300°C or higher). In this case, thermal treatment is carried out such that the crystallization degree of the amorphous carbon particles does not exceed that of the graphitic particles. The thermally treated amorphous carbon particles exhibit electrical conductivity higher than that of amorphous carbon particles which have not undergone thermal treatment. In addition, the thus-treated amorphous carbon particles are envisaged to exhibit preferred effects; for example, the particles can be formed into a product exhibiting enhanced coating strength.

[0049]

(Graphitic particles)

The graphitic particles employed in the present invention are not necessarily graphitized completely. Specifically, the graphitic particles may be graphitized such that the interplanar spacing C_0 (i.e., twice the distance between carbon-network layers (d_{002})) as measured through X-ray diffractometry is about 0.685 nm or less (i.e., d_{002} is 0.3425 nm or less). The theoretical C_0 value of completely graphitized graphite is known to be 0.6708 nm (i.e., d_{002} is 0.3354 nm), and the graphitic particles are considered not to have a C_0 value lower than the theoretical C_0 value.

[0050]

The graphitic particles may be formed of natural

graphite or artificial graphite. Alternatively, the graphite particles may be formed through thermal treatment of a carbonaceous raw material.

The raw material of the graphitic particles may be carbonaceous powder such as natural graphite, artificial graphite, coke, mesophase carbon, pitch, wood charcoal, or resin charcoal. Of these, preferred examples are natural graphite; artificial graphite; and coke, mesophase carbon, and pitch, which are easily graphitized through heating. When the graphitic particles assume a shape which approximates the sphere, the particles are readily kneaded in a resin, and fluidity of the particles in the resin is improved. Therefore, when the graphitic particles formed of mesophase carbon is added to a resin, the resultant resin exhibits excellent moldability.

[0051]

The graphitic particles and the amorphous carbon particles may be milled in advance in order to attain a finally required particle size, or may be milled after thermal treatment. Preferably, these particles are milled in advance in order to attain a required particle size.

The graphitic particles and the amorphous carbon particles may be milled by use of, for example, a high-speed rotation mill (a hammer mill, a pin mill, or cage mill), a ball mill (a rotation mill, a vibration mill, or a planetary mill), or a stirring mill (a beads mill, an attritor, a flow-tube mill, or an annular mill). Under certain conditions, an

atomizer such as a screen mill, a turbo mill, a super micron mill, or a jet mill may be employed.

[0052]

In consideration of characteristics and productivity, the average particle size of the graphitic particles is preferably 0.1 to 100 μm , more preferably 0.1 to 80 μm . Preferably, the graphitic particles have an average particle size of 0.1 to 80 μm . More preferably, the graphitic particles contain substantially no particles having a size of 0.5 μm or less and/or substantially no particles having a size of more than 80 μm ; i.e., the graphitic particles contain particles having such sizes in a total amount of 5 mass% or less, preferably 1 mass% or less.

[0053]

In a thermal treatment process, at least one species selected from among boron, nickel, cobalt, manganese, silicon, magnesium, aluminum, calcium, titanium, vanadium, chromium, iron, copper, molybdenum, tungsten, zirconium, and a compound thereof, each species having an average particle size of 0.1 to 100 μm , is added to and mixed with carbonaceous powder (raw material powder) [graphitic particles and amorphous particles] having an average particle size of 0.1 to 100 μm , such that the amount of each species is 0.01 to 10 mass%, preferably 0.1 to 10 mass%, on the basis of the entirety of the raw material powder; and the resultant mixture is placed in a graphite-made container having a lid (e.g., a crucible). When the amount of the aforementioned compound is less than

0.01 mass%, the effect of the compound is insufficient, whereas when the amount of the compound exceeds 10 mass%, the effect almost saturates and thus further effect commensurate with the increased amount is not obtained, possibly raising problems such as aggregation of the compound powder and the carbonaceous powder.

[0054]

In order to cause an element of interest to be present in the graphitic particles in an amount of 100 mass ppm or more after thermal treatment, more effectively, at least one compound powder is added to and mixed with the graphitic particles (for example, when boron is to be present in the graphitic particles, for example, boron, boron carbide, or boron oxide is added to the particles). The reason for the above is as follows: when a mixture of substances having different melting points and boiling points is employed, variation of the temperature in a furnace during the course of thermal treatment can be reduced.

[0055]

In order to carry out thermal treatment, the graphite-made container containing the raw material and the aforementioned compound is heated in an atmosphere of an inert gas such as argon, nitrogen, or helium. The furnace employed for thermal treatment may be a general graphitization furnace such as an Acheson furnace or a high-frequency induction heating furnace. Thermal treatment is preferably carried out at 2,000°C or higher and at a

temperature such that the aforementioned added substance or a generated boride is not evaporated and lost. The heating temperature is preferably regulated to about 2,000 to about 2,500°C. During the course of thermal treatment, graphitization of the raw material which has not been graphitized proceeds. In the present invention, the aforementioned added substance effectively serves as a graphitization catalyst. When thermal treatment is carried out at 2,500°C or higher; for example, at 2,500 to 3,200°C, graphitization of the graphitic particles advantageously proceeds. However, in consideration of the material of the thermal treatment apparatus, the upper limit of the thermal treatment temperature is 3,200°C or thereabout.

[0056]

The amount of the graphitic particles contained in the carbonaceous material for forming an electrically conductive composition is 7 to 65 mass%, preferably 15 to 30 mass%, more preferably 15 to 25 mass%.

When an electrically conductive coating material having a volume resistivity of 0.1 Ω cm or less is required, the carbonaceous material for forming an electrically conductive composition preferably contains boron-containing vapor grown carbon fiber rather than vapor grown carbon fiber. In this case, the amount of the boron-containing vapor grown carbon fiber contained in the carbonaceous material is 60 mass% or more, preferably 75 mass% or more, more preferably 80 mass% or more; and the total amount of the amorphous carbon

particles and/or the graphitic particles contained in the carbonaceous material is 40 mass% or less, preferably 25 mass% or less, more preferably 20 to 10 mass%.

[0057]

Since each fiber filament of vapor grown carbon fiber contains a hollow space along the filament, the carbon fiber exhibits excellent thermal conductivity, and is suitable for use in, for example, a paste requiring thermal conductivity. When the vapor grown carbon fiber is employed in a coating film, the strength and electrical conductivity of the film are enhanced. When the vapor grown carbon fiber is thermally treated or boron is incorporated into the carbon fiber, the resultant carbon fiber exhibits enhanced crystallinity and electrical conductivity, whereby oxidation resistance of the carbon fiber is improved, and long-term stability is imparted to the carbon fiber.

Even when either the graphitic particles or the amorphous carbon particles are employed, wettability of the electrically conductive composition is enhanced, electrical conductivity anisotropy attributed to the vapor grown carbon fiber is prevented, and a coating film formed from the composition exhibits low kinetic friction coefficient and excellent tribological characteristics. When the graphitic particles or the amorphous carbon particles (i.e., carbonaceous substance) are subjected to heating treatment or boronization treatment, the resultant particles are envisaged to exhibit effects similar to those obtained from the vapor

grown carbon fiber. Even when either the graphitic particles or the amorphous carbon particles are employed, the above-described effects are obtained. However, when the graphitic particles and the amorphous carbon particles are employed in combination, these particles exhibit effects as described below. The amorphous carbon particles, having an irregular, branched-chain structure, come into contact with the vapor grown carbon fiber, to thereby form an electrical network, whereby electrical conductivity is obtained. In addition, the graphitic particles, which exhibit electrical conductivity higher than that of the amorphous carbon particles, are dispersed in micropores present between fiber filaments of the carbon fiber, and thus the electrical network is further spread, and lowering of electrical conductivity, which is caused by separation of fiber filaments which are in contact with one another, is prevented, whereby electrical conductivity is envisaged to be obtained in a consistent manner.

[0058]

(Resin component)

The electrically conductive composition of the present invention contains a resin component as a binder or a matrix. Examples of the resin component which may be employed include thermoplastic resins, thermosetting resins, and thermoplastic elastomers.

[0059]

Examples of the thermoplastic resins include

polyethylene (PE), polypropylene (PP), polymethylpentene, polybutene, polybutadiene, polystyrene (PS), styrene butadiene resin (SB), polyvinyl chloride (PVC), polyvinyl acetate (PVAc), polyethyl methacrylate (PMMA, acrylic resin), polyvinylidene chloride (PVDC), polytetrafluoroethylene (PTFE), an ethylene-polytetrafluoroethylene copolymer (ETFE), an ethylene-vinyl acetate copolymer (EVA), AS resin (SAN), ABS resin (ABS), an ionomer (IO), AAS resin (AAS), ACS resin (ACS), polyacetal (POM, polyoxymethylene), polyamide (PA, nylon), polycarbonate (PC), polyphenylene ether (PPE), polyethylene terephthalate (PETP), polybutylene terephthalate (PBTP), polyarylate (PAR, U polymer), polysulfone (PSF), polyether sulfone (PESF), polyimide (PI), polyamideimide (PAI), polyphenylene sulfide (PPS), polyoxybenzoyl (POB), polyether ether ketone (PEEK), polyether imide (PEI), cellulose acetate (CAB), and cellulose acetate butyrate (CAB). Of these, polyethylene, polypropylene, polyvinyl chloride, polyethyl methacrylate, polytetrafluoroethylene, and an ethylene-polytetrafluoroethylene copolymer are preferred. These thermoplastic resins may be employed singly or in combination of two or more species.

[0060]

Examples of the thermosetting resins include phenolic resin (PF), amino resin, urea resin (UF), melamine resin (MF), benzoguanamine resin, unsaturated polyester (UP), epoxy resin (EP), diallyl phthalate resin (allyl resin) (PDAP), silicone (SI), polyurethane (PUR), and vinyl ester resin. Of these,

phenolic resin, unsaturated polyester resin, epoxy resin, and vinyl ester resin are preferred. If desired, one or more species of the thermoplastic resins and one or more species of the thermosetting resins may be employed in combination.

[0061]

Examples of the thermoplastic elastomers include styrene-butadiene elastomer (SBC), polyolefin elastomer (TPO), urethane elastomer (TPU), polyester elastomer (TPEE), polyamide elastomer (TPAE), 1,2-polybutadiene (PB), polyvinyl chloride elastomer (TPVC), and an ionomer (IO). Of these, polyolefin elastomer, polyamide elastomer, polyester elastomer, and an ionomer are preferred. If desired, one or more species of the thermoplastic elastomers and one or more species of the thermoplastic or thermosetting resins may be employed in combination.

[0062]

(Composition)

The proportion of the thermoplastic resin, thermosetting resin, or thermoplastic elastomer contained in the electrically conductive composition of the present invention is generally 20 to 95 mass%, preferably 40 to 65 mass%. When the amount of the resin component is less than 20 mass%, even if an electrically conductive path is formed from the electrically conductive composition, exfoliation of the conductive path tends to occur, whereas when the amount of the resin component is 95 mass% or more, the electrically conductive composition may fail to exhibit sufficient

electrical conductivity.

[0063]

The electrically conductive composition of the present invention may contain a known additive, so long as the additive does not impede the purposes of the present invention. Examples of the additive include a plasticizer, a stabilizer, a filler, a reinforcing agent, an antioxidant, an ultraviolet absorber, a flame retardant, and a lubricant. The additive to be employed is appropriately determined in accordance with use of the electrically conductive composition of the present invention.

[0064]

The electrically conductive composition of the present invention is produced by mixing the vapor grown carbon fiber, the amorphous carbon particles, the graphitic particles, and the resin component. These components may be mixed by use of a known mixer. No particular limitations are imposed on the order of mixing of the components. The electrically conductive composition may be prepared into an electrically conductive coating material or an electrically conductive adhesive by means of a known method.

[0065]

The electrically conductive composition of the present invention exhibits excellent electrical conductivity. Therefore, the electrically conductive composition can be formed into an electrically conductive coating material or an electrically conductive ink. Since the electrically

conductive composition contains the resin component serving as a matrix, the composition exhibits moldability. When the electrically conductive composition is appropriately molded into a product, the thus-molded product can be employed in, for example, a low-resistance band for a facsimile electrode plate, etc., an antistatic conveyer belt, a medical rubber product, an electrically conductive tire, an IC accommodating case, a copying or spinning roll, an elastic electrode, a heating element, an element for prevention of overcurrent or overheat, an electromagnetic wave shielding material, a keyboard switch, a connector element, and a switching element.

[0066]

The solvent employed in the present invention may be a solvent which is generally employed in an electrically conductive coating material or an electrically conductive adhesive. Examples of the solvent which may be employed include methyl ethyl ketone, N-methylpyrrolidone, a terpene compound such as terpineol, glycol ether, and glycol ester.

[0067]

Preferably, a solvent exhibiting good solubility with respect to the resin component to be employed is selected from among the aforementioned solvents. These solvents may be employed singly or in combination of two or more species. No particular limitations are imposed on the amount of the solvent to be employed, and a necessary amount of the solvent is the amount that is generally required for producing a coating material or an adhesive.

[0068]

In order to enhance fluidity of the conductive composition during the course of application, and the strength and tribological characteristics of a coating film formed through application of the composition, the composition may contain an auxiliary agent (e.g., a dispersant or a thickener) which is generally employed in an electrically conductive coating material. Dispersion of the electrically conductive material, etc. into a varnish may be carried out by means of a method which is generally employed for preparing an electrically conductive coating material.

[0069]

The incorporation amounts of the electrically conductive material, auxiliary agent, and resin employed in the present invention vary with the characteristics of the resin, and are determined in accordance with characteristics (e.g., electrical conductivity, viscosity, and fluidity) required for the resultant electrically conductive coating material or electrically conductive adhesive.

[0070]

When a mass%, b mass%, and c mass% represent the amounts of the vapor grown carbon fiber, the graphitic particles, and the amorphous carbon particles contained in the electrically conductive composition, with the proviso that the solvent being excluded from the composition, respectively, a, b, and c preferably satisfy the following relations:

$5 \leq a + b + c \leq 80$, $1 \leq a \leq 60$, $1 \leq b \leq 60$, and $1 \leq c \leq 30$.

In order to enhance the volume resistivity of the electrically conductive composition, the vapor grown carbon fiber may contain boron-containing vapor grown carbon fiber, which is carbon fiber of high electrical conductivity. In order to efficiently form an electrically conductive path, the boron-containing vapor grown carbon fiber is incorporated into the electrically conductive composition in an amount of preferably 10 to 60 mass%, more preferably 20 to 60 mass%, on the basis of the entirety of the composition, with the proviso that the solvent being excluded from the composition.

[0071]

When a mixture of the vapor grown carbon fiber and the graphitic particles or a mixture of the vapor grown carbon fiber and the amorphous carbon particles is employed, the vapor grown carbon fiber is preferably a vapor grown carbon fiber containing boron in an amount of 0.01 to 5 mass%, each fiber filament of the carbon fiber containing a hollow space along the filament in its interior, and having a multi-layer structure, an outer diameter of 2 to 500 nm, and an aspect ratio of 10 to 15,000. The amount of the boron-containing vapor grown carbon fiber contained in the electrically conductive composition is preferably 20 mass% or more, more preferably 25 to 60 mass%, much more preferably 30 to 50 mass%. When the amount of the vapor grown carbon fiber is less than 20 mass%, an electrically conductive path is not

formed by the vapor grown carbon fiber, and an aimed electrical conductivity fails to be obtained.

[0072]

(Use)

No particular limitations are imposed on the object to which the electrically conductive coating material or the electrically conductive adhesive is applied, so long as the resultant coating film requires electrical conductivity. In particular, the electrically conductive coating material is suitable for use in production of an electric circuit board such as a printed wiring board.

The thus-produced electric circuit board is employed in a variety of products; for example, household electrical appliances, industrial products, vehicles, communication information products, airplanes and ships, products employed in the cosmic space, weapons, clocks, cameras, and toys.

[0073]

Depending on use of the electric circuit board, the electric circuit for wiring formed from the electrically conductive coating material or the electrically conductive ink may be provided on one surface or both surfaces of the board. The electric circuit board is produced through, for example, the following procedure: the electrically conductive coating material is applied onto a substrate through printing or coating; and if desired, the coating material is cured by means of heat or an electron beam, or the coating material is dried for removing the solvent. The thickness of a coating

film formed from the electrically conductive coating material is generally 5 to 100 μm .

[0074]

[Examples]

The present invention will next be described in more detail with reference to representative examples, which should not be construed as limiting the invention thereto.

[0075]

(Production of vapor grown carbon fiber)

Vapor grown carbon fiber, fiber filaments of the carbon fiber having an average diameter of 150 nm and an average length of 20 μm , were produced by means of the method disclosed in Japanese Patent No. 2778434. The thus-produced carbon fiber was thermally treated in an argon atmosphere at 1,000°C, and then graphitized at 2,800°C (hereinafter, the resultant product will be called "VGCF(150)").

In a manner similar to that described above, vapor grown carbon fiber, fiber filaments of the carbon fiber having an average diameter of 80 nm and an average length of 20 μm , was produced. The thus-produced carbon fiber was thermally treated in an argon atmosphere at 1,000°C, and then graphitized at 2,800°C (hereinafter, the resultant product will be called "VGCF(80)").

[0076]

(Production of VGCF-B)

Vapor grown carbon fiber, fiber filaments of the carbon fiber having an average diameter of 150 nm and an average

length of 20 μm , was thermally treated in an argon atmosphere at 1,000°C. Subsequently, boron carbide (2 mass%) was added to the carbon fiber, followed by graphitization at 2,800°C (hereinafter, the resultant product will be called "VGCF-B(150)").

Vapor grown carbon fiber, fiber filaments of the carbon fiber having an average diameter of 80 nm and an average length of 20 μm , was thermally treated in an argon atmosphere at 1,000°C. Subsequently, boron carbide (2 mass%) was added to the carbon fiber, followed by graphitization at 2,800°C (hereinafter, the resultant product will be called "VGCF-B(80)").

[0077]

(Production of CB-H)

Carbon black (Ketjenblack EC, product of Akzo) was thermally treated in an argon atmosphere at 2,800°C (hereinafter, the resultant product will be called "CB-H(K)").

[0078]

(Production of CB-B)

Boron carbide (2 mass%) was added to carbon black (Ketjenblack EC, product of Akzo), followed by thermal treatment in an argon atmosphere at 2,800°C (hereinafter, the resultant product will be called "CB-B(K)").

[0079]

(Production of graphitic particles-B)

Boron carbide whose average particle size had been regulated to 10 μm (2 mass%) was added to UFG10 (artificial

graphite fine powder produced by Showa Denko K.K., average particle size: 5 μm), to thereby prepare a mixture sample. The mixture sample was placed in a graphite-made container having a lid, and then thermally treated in an argon atmosphere at 2,800°C (hereinafter, the resultant product will be called "UFG10-B").

[0080]

(Example 1)

A xylene-modified phenoxy resin serving as a resin component, glycol ether serving as a solvent, graphitic particles (UFG10, artificial graphite fine powder produced by Showa Denko K.K., average particle size: 5 μm) serving as an electrically conductive material, amorphous carbon particles (Ketjenblack EC, product of Akzo) (hereinafter called "CB(K)"), and vapor grown carbon fiber (average diameter of fiber filaments of the carbon fiber: 150 nm, average length of the filaments: 20 μm) (hereinafter called "VGCF(150)") (the amounts of the graphitic particles, amorphous carbon particles, and vapor grown carbon fiber are shown in Table 1) were kneaded by use of a three roll mill, to thereby prepare an electrically conductive paste.

The thus-prepared paste was applied through screen printing to an epoxy substrate, to thereby form films ($n = 5$), each having a pattern (width: 4 mm, length: 10 mm), and the thus-patterned films were dried and cured at 200°C. Each of the resultant patterned films was found to have a thickness of 10 μm . The volume resistivity of the patterned film was

measured. The average volume resistivity is shown in Table 1.

[0081]

(Examples 2 through 12, Comparative Examples 1 through 5)

In a manner similar to that of Example 1, an electrically conductive paste was prepared from the materials shown in Table 1 or 2 (i.e., vapor grown carbon fiber, and graphitic particles and/or amorphous carbon particles). A patterned film for evaluation was formed from the paste through printing, and then dried and cured. The volume resistivity of the resultant film was measured.

[0082]

[Table 1]

Amount (mass%) (on the basis of dried and cured paste)

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Carbon fiber	VGCF(150) VGCF-B(150) VGCF-B(80)	10	10	10	10	10	20	30	45
Carbon black	CB(K) CB-H(K) CB-B(K)	10	10	10	10	10	5	5	10
Graphite	UFG10 UFG10-B	20	20	20	20	20			
Evaluation	Volume resistivity Ωcm	0.6	0.4	0.3	0.5	0.4	0.4	0.1	0.015

[0083]

[Table 2]

Amount (mass%) (on the basis of dried and cured paste)

		Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Carbon fiber	VGCF(150) VGCF-B(150) VGCF-B(80)	45	45	45				45	45
Carbon black	CB(K) CB-H(K) CB-B(K)	10				10	10		
Graphite	UFG10 UFG10-B		10	10	20	20			
Evaluation	Volume resistivity Ωcm	0.025	0.04	0.03	2	1	1.2	0.3	0.08

[0084]

[Effects of the Invention]

The present invention provides an electrically conductive coating material or an electrically conductive adhesive, which contains, as an electrically conductive material, a mixture of vapor grown carbon fiber, graphitic particles, and amorphous carbon particles, or a mixture of vapor grown carbon fiber containing boron in an amount of 0.01 to 5 mass%, and graphitic particles or amorphous carbon particles. When an electrically conductive product (e.g., a coating film) is formed from the electrically conductive coating material or electrically conductive adhesive, the resultant product exhibits enhanced electrical conductivity, oxidation resistance, long-term stability, and tribological characteristics, and lowered resistance anisotropy.